PB82-196155

Sodium Fluxing and In-situ Glassification for Hazardous Materials Disposal

MSA Research Corp.
Evans City, PA

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

Feb 82

U.S. Department of Commerce
National Technical Information Service
NTIS

EPA-600/2-82-021
February 1982

PB82-196155

SODIUM FLUXING AND IN-SITU GLASSIFICATION FOR HAZARDOUS MATERIALS DISPOSAL

by

J.S. Greer
G.H. Griwatz
S.S. Gross
R.H. Hiltz
MSA Research Corporation
Division of Mine Safety Appliances Company
Evans City, Pennsylvania 16033

Contract 68-03-2492

Project Officer

John E. Brugger
Oil and Hazardous Materials Spill Branch
Municipal Environmental Research Laboratory (Cincinnati)
U.S. Environmental Protection Agency
Edison, New Jersey 08837

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-82-021	ORD Report	

4. TITLE AND SUBTITLE	5. REPORT DATE
SODIUM FLUXING AND IN-SITU GLASSIFICATION FOR HAZARDOUS MATERIALS DISPOSAL	March 1982
	6. PERFORMING ORGANIZATION CODE: AC-957

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
J.S. Greer, G.H. Griwatz, S.S. Gross and R.H. Hiltz	MSAR 80-14

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
MSA Research Corporation Division of Mine Safety Appliances Co. Evans City, Pennsylvania 16033	1BB610;AZb1B-DU-B-113
	11. CONTRACT/GRANT NO.: 68-03-2492

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Municipal Environmental Research Laboratory - Cin., OH Office of Research and Development U. S. Environmental Protection Agency Cincinnati, OH 45268	Final. 2/11/77-1/11/80
	14. SPONSORING AGENCY CODE: EPA/600/14

15. SUPPLEMENTARY NOTES

Project Officer: John E. Brugger (201)321-6634

16. ABSTRACT

Toxic wastes have become a prime consideration in the maintenance of the ecology. Numerous materials of commerce, being unsuitable for landfill and resistance to thermal degradation, pose problems in disposal. The U.S. Environmental Protection Agency instituted a project to evaluate new approaches to the ultimate disposal of such materials. The study reported here, one segment of the major project , was instituted to assess two innovative techniques--in situ glassification and reactive degradation using liquid sodium.

The glassification technique experienced success in the encapsulation of toxic materials. Because of the need for very high reaction temperatures, however, small but significant quantities of the toxic material were vented during reaction.

The utilization of a molten sodium medium to thermally degrade toxic materials to products acceptable for direct disposal or recovery was successfully demonstrated. Based upon the data derived and the existing state-of-the-art, a practical system to employ this technique for ultimate disposal appears feasible.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
waste disposal glass sodium hazardous materials fluxes	toxic wastes ultimate disposal glassification liquid sodium degradation	13B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	29
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

DISCLAIMER

This report has been reviewed by the Municipal Environment Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This work is directed to the development of new procedures for the ultimate disposal of hazardous materials. One phase investigates a unique approach to the encapsulation of toxic wastes within a glass matrix. A second phase evaluates the use of molten sodium to thermally decompose toxic materials to innocuous products.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

Toxic wastes have become a prime consideration in the maintenance of the ecology. Numerous materials of commerce, being unsuitable for landfill and resistant to thermal degradation, pose problems in disposal. The U.S. Environmental Protection Agency instituted a project to evaluate new approaches to the ultimate disposal of such materials. The study reported here, one segment of the major project, was instituted to assess two innovative techniques -- in-situ glassification and reactive degradation using liquid sodium.

The glassification technique experienced success in the encapsulation of toxic materials. Because of the need for very high reaction temperatures, however, small but significant quantities of the toxic material were vented during reaction.

The utilization of a molten sodium medium to thermally degrade toxic materials to products acceptable for direct disposal or recovery was successfully demonstrated. Based upon the data derived and the existing state-of-the-art, a practical system to employ this technique for ultimate disposal appears feasible.

This report was submitted in fulfillment of Contract No. 68-03-2492 by MSA Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period February 11, 1977 to January 11, 1980 and work was completed June 1981.

CONTENTS

Foreword iii
Abstract iv
Figures v
Tables v

1. Introduction 1
2. Conclusions & Recommendations 2
3. Glassification Study 4
   Background 4
   Test Procedure 4
   Evaluation of Material Encapsulation 13
4. Liquid Sodium Reactions 15
   Background 15
   Experimental Technique 15
   Test Results 17

FIGURES

Number		Page
1	Glassification reaction vessel	5
2	Experimental reactor and analysis systems	16

TABLES

Number		Page
1	Initial Glassification Compositions	8
2	Glassification Reactions Using KO_2	9
3	Glassification Reactions Using Aluminum Powder	9
4	Modifications for Slower Reaction Rates	11
5	Additional Tests on Slow Reacting Compositions	12
6	Test Data Collected from Reactions of Hazardous Materials with $\sim$1000 g Liquid Sodium in Stainless Steel Reactor Vessel	18

SECTION 1

INTRODUCTION

As technology for the control and cleanup of hazardous material spills has evolved, the volume and types of materials that must be disposed has increased commensurately. Difficulties have arisen in the disposal of certain hazardous material categories. The shortcomings of landfill disposal have been quite evident. Incineration is more reliable, but it is not adaptable to all hazardous chemicals.

The existing situation has led the U.S. Environmental Protection Agency to investigate alternative procedures for the ultimate disposal of hazardous chemicals. As part of this general investigation, a contract was awarded to MSA Research Corporation to conduct a laboratory feasibility study of two procedures -- sodium metal fluxing and glassification -- for ultimate disposal. Both procedures had sufficient background to justify the investigation. The ability of molten sodium to degrade organic compounds and to form compounds with other elements is well known. The process has never been investigated as a disposal technique, however.

The encapsulation of materials in a glass matrix has been under investigation for some time as a disposal technique. The approach to date has been to disperse the material to be disposed in a molten glass phase. The process could be considered reasonably successful except that the dispersed material is not always totally encapsulated. Since dispersion cannot be accomplished on a micro scale, networks of the contained phase can persist to the surface of the total mass.

The work to be presented in this report concerns (1) the investigation of the in-situ formation of glass from basic components interspersed with the materials to be encapsulated and (2) a laboratory study of the use of molten sodium as a mechanism for degrading a range of hazardous materials to yield a disposable product. The sodium fluxing process was successfully demonstrated for several categories of material. The glassification study, although technically successful, experienced some undesirable side effects.

SECTION 2

CONCLUSIONS & RECOMMENDATIONS

It was established that a glass phase can be developed through in-situ pyrochemical reactions. Certain materials can be incorporated into the glass matrix during its formation with good resistance to extraction by leaching at least to 25% by volume. These materials include lead, chromium, and copper. The elements arsenic and antimony are less well bound. The intermetallic cadium selenide interfered with glass formation. It is uncertain which of the two elements is responsible. Since cadium does not appear strongly in the leachate whereas selenium does, it would appear that selenium is the basic interferant.

The utility of this pyrochemical system is compromised by the fact that particulate matter containing the toxic compound is released during reaction. The amount lost is small by comparison to the total volume of reactants, but it does not appear to be a tolerable situation. Mechanisms that might alleviate the material loss problem were identified but not pursued.

The interactions of six representative hazardous materials with molten sodium indicate that such reactions can provide the basis for the disposal of many unmanageable waste materials. The results of these tests show that most hazardous materials react with excess sodium to form innocuous salts, carbon, and free metals, with the release of nitrogen and hydrogen as gases. The more complex compounds proceed through a series of intermediate reaction products but ultimately degrade to the basic products. This was observed in tests with 2-chloro-4-phenyl phenol, kepone, and parathion. Hydrogen is found in the recirculating cover gas stream as a product of the reaction of absorbed moisture as well as the degradation of waste materials. Although nitrogen is also expected to appear as a released gas, this was not observed with parathion, which has a nitro substituent.

The products of these reactions--salts, heavy metals, and free carbon--can be separated by combinations of filtering, cold-trap filtering, solvent extraction and/or vacuum distillation. They could be removed as relatively pure materials for recycling or as innocuous waste products that can be handled by standard disposal procedures.

The potential of the sodium system for degrading essentially pure materials has been established. It is reasonably certain that using state-of-the-art technology and equipment, a system could be evolved of commercial size. It must be recognized, however, that sodium metal fluxing appears to be applicable to either pure materials or waste materials wherein the toxic substances is the principal constituent. Inert materials, soil and the like,

do not interfere with the fluxing process but they are expected to load up the filtration and cold trap systems. This causes abnormal maintenance and system down time.

The use of in-situ glassification also has merit. It appears reasonable to consider scaleup of the existing processes to determine exactly how problematic the observed loss of material will be.

Some investigation of gasless pyrochemical processes is also warranted. Although the known systems may not be amenable to glass formation, the clinker which is formed may be acceptable or possibly glass forming materials might be successfully added without compromising the pyrochemical reaction.

Like sodium fluxing, glassification appears to be best applied to waste materials where the concentration of inert material is low.

SECTION 3

GLASSIFICATION STUDY

BACKGROUND

The use of glass encapsulation to entrain toxic or radioactive materials for safe disposal has seen extensive development. Although several procedures have evolved, they all essentially blend the chemical to be disposed into a molten glass matrix. The basic drawback is the difficulty of entraining the material for disposal as a discontinuous phase. Through gross segregations or semicontinuous areas, a path to the surface occurs for the encapsulated material to be leached with long-term exposure to the environment. This action is exaggerated if cracking or other failures occur in the glass.

This difficulty could be minimized by effecting dispersion of the encapsulated phase on a micro scale. This can be approached by using a large volume ratio of glass to material for disposal. An alternative procedure, which would result in less disposal volume, appears possible if the glass phase could be formed in-situ. The material to be disposed would be blended on a micro scale with glass-forming components which would be pyrochemically reacted to form the glass. This procedure would ensure uniformity of the final mass and tend to entrain the hazardous material as discrete particles.

The formation of glass during a pyrochemical reaction has been demonstrated in prior MSA studies (1). During the development of a pyrochemical system to generate CO_2, reabsorption of the gas by the reaction residue created an undesirable situation. By incorporating borates and other materials in the mix the reaction residue was converted to a glass thus eliminating the reabsorption problem. This work was used as the basis for beginning this study to investigate in-situ glassification as a mechanism for encapsulating hazardous materials for subsequent safe disposal.

TEST PROCEDURE

The test phase was begun by evaluating the glass reaction previously developed for the CO_2 generating composition. Small compacts were used weighing 10 grams (0.35 oz) pressed at 1000 psi to pellets 3.8 cm (1.5 in.) in diameter by 1.9 to 2.5 cm (0.75 to 1 in.) in height. The pellets were placed in a ceramic cup on a base in a reaction vessel shown in Figure 1. In these and all subsequent tests a starter pellet of sodium chlorate was used to initiate the glassification reaction. An electric match and flash paper ignited the starter pellet.

(1) Carbon dioxide generating compositions, U.S. Patent 3,477,955.

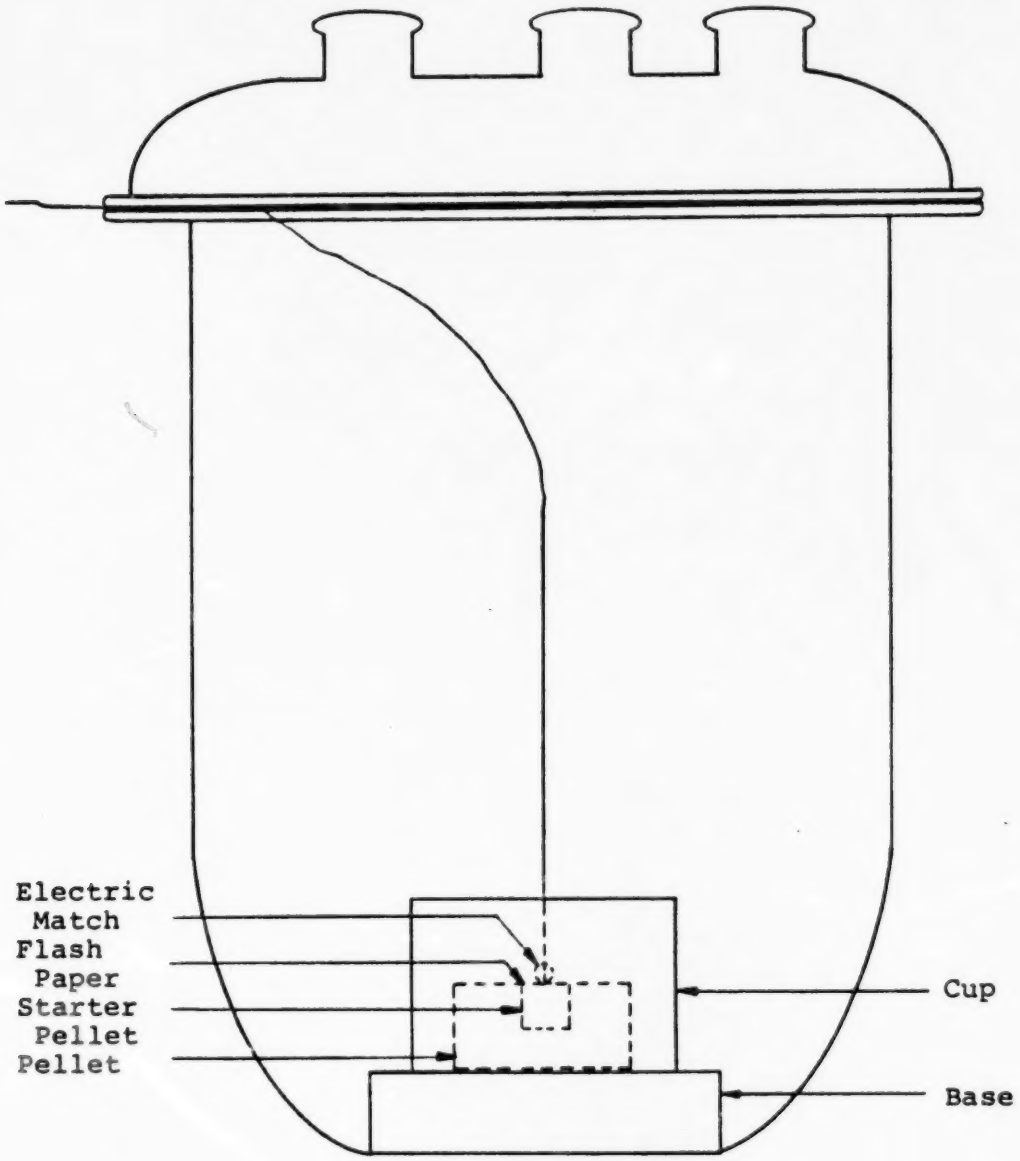


Figure 1. Glassification reaction vessel

The basic CO_2 reactions are given in Equations 1 and 2:

$$10\ KO_2 + 3\ CaC_2 \longrightarrow 6\ CO_2 + 3\ CaO + 5\ K_2O \quad (1)$$

$$5\ Na_2O_2 + CaC_2 \longrightarrow 2\ CO_2 + CaO + 5\ Na_2O \quad (2)$$

These two formulations, containing the following percentages of reactants with SiO_2, were ignited:

10%	CaC_2	6%	CaC_2
47%	KO_2	48%	Na_2O_2
43%	SiO_2	45%	SiO_2

The intention was that the reactants would supply the heat, while the SiO_2 would from the glass phase. An amount in excess of the stoichiometric requirements of the oxidizing agents KO_2 and Na_2O_2 was used to increase the chances of a successful glassification reaction.

The pellets did not react. The amount of SiO_2 had to be decreased by one-half before a reaction would occur. Even then, a cinder residue rather than a glass resulted from the reaction. The cinder fell apart rapidly when placed in water.

It was felt that the above reactants would not produce a glassified product. Two reasons could be advanced to explain the observed behavior. First, the reaction was not producing enough heat to reach the glassification temperatures of 800°C (1472°F). Second, the production of CO_2 created a porous reaction product which lacked integrity. It was concluded that higher temperature pyrochemical reactions were needed; one which was either a solid state reaction or one which did not produce any gas.

Solid pyrochemical systems produced commercially by MSA based upon sodium chlorate were examined. The purpose of the commercial system is to produce large quantities of oxygen through the thermal dissociation of sodium chlorate. Small amounts of iron powder are added to react with some of the oxygen. The oxidation of the iron provides heat to continue the thermal dissociation of the sodium chlorate. Silica and barium peroxide are added to prevent oxygen from being reabsorbed. For the tests conducted in this program the amount of iron powder was increased to consume as much oxygen as possible.

A typical composition pressed at 1000 psi into a 3.8 cm (1.5 in.) diameter pellet for testing contained:

30%	iron powder	25%	silica
15%	barium peroxide	30%	sodium perchlorate

The reaction produced a good coherent cinder but no glass was formed based upon visual examination. It was clear that the use of iron as a fuel does not result in a glassified product.

In the next series of tests the iron powder was replaced with silicon powder to enhance glass formation through the oxidation of the silicon to silicon dioxide. In some of the tests glass fibers were used to replace the silica powder to improve compact integrity prior to reacting the pressed mass. Some compositions formed glass; however none of the reacted masses were considered satisfactory. The chemical compositions and character of the reacted samples are given in Table 1.

Although the reactions were achieving temperatures where glassification could occur, the crystalline sodium chloride which was being formed was an impediment to the formation of a continuous glass phase. Additionally, it was doubtful that a compact containing sodium chloride as a result of the pyrochemical reaction would be resistant to leaching.

Possible replacements were examined for the sodium chlorate. Potassium dioxide (KO_2) was selected as a substitute. Upon decomposition it releases oxygen to form K_2O. This compound should be compatible with glass formation.

A series of tests were run with potassium dioxide substituted for sodium chlorate. The potassium dioxide levels were gradually increased due to the possibility of violent reaction. The compositions tested are given in Table 2. Although there was evidence of some glass formation, the reaction products were primarily a cinder-like material.

Modification of the pyrochemical reaction was shifted from the oxidizer to the fuel. Analysis of the metals found in commercial glass suggested the use of aluminum as a substitute for silicon in whole or part.

Several tests were conducted replacing some of the silicon with aluminum powder. The compositions are shown in Table 3. As in previous tests, changes in levels of oxidizing agents or fuels were done slowly due to possible violent reactions.

Except for the edges of the pellet the fourth composition exhibited good glass formation. This composition provided a basis for further modifications for a glass-producing reaction.

Good glass formation was found predominantly in the interior of the pellet. Initial improvement in this glass-producing formulation appeared to be in enhancing glass formation at the pellet surface. Glass wool was used to insulate the pellet and significantly increased the amount of glass formation on the exterior of the pellet. Preventing heat loss helped maintain a uniform pellet temperature during reaction and cool down.

Attempts to produce a better product through increases in the percentage of glass fiber or barium dioxide and/or decreases in the amount of potassium dioxide all resulted in a poorer quality product. The substitution of the glass fibers for silica powder did increase the quantity of glass in the product. The best glassification in this series of tests was achieved using a composition of 20% aluminum, 40% potassium dioxide, 15% barium oxide and 25% silica/glass fibers.

TABLE 1. INITIAL GLASSIFICATION COMPOSITIONS

Sample No.	Compositions (%)						Results
	Iron powder	Silicon powder	Barium peroxide	Silica	Glass fibers	Sodium chlorate	
1	15	15	15	25		30	Coherent product but no glass
2		30	10			60	Very hot reaction; possibly some glass
3		30	10	20		40	Coherent product but no glass
4		30			20	50	Reaction only around starter pellet
5		23.6			16.4	60	" " "
6		30			10	60	" " "
7		25	10		10	55	Possibly some glass formed around edges
8		20	5		25	50	Reaction only around insert
9		20	10		20	50	Reaction temperature 1100°C (2012°F); poor product
10		20	15		35	30	Poor product
11		20	15	10	25	30	" "
12		10	15	20	25	30	" "
13		20	10	10		60	
14		10	10	20		60	Reaction only around insert
15			15	30		55	" " " "

TABLE 2. GLASSIFICATION REACTIONS USING KO_2

Sample No.	Compositions (%) Silicon powder	Barium peroxide	Silica	Glass fibers	Sodium chlorate	Potassium dioxide	Results
1	20	10	10		50	10	Coherent product; no glass
2	20	10	10		40	20	Possibly some glass
3	10	10		30	30	20	Possibly some glass
4	10	10		50		30	Possibly some glass
5	20	10		40		30	Possibly some glass
6	20	10	20	30	40	40	Temperature > 1100°C (> 2012°F); possibly some glass

TABLE 3. GLASSIFICATION REACTIONS :USING ALUMINUM POWDER

Sample No.	Compositions (%) Silicon powder	Aluminum powder	Glass fibers	Barium dioxide	Potassium dioxide	Results
1	10	5	50	5	30	Some glass formation
2	10	10	50	10	20	No glass
3	10	10	40	10	30	No glass
04	15	15	30	10	30	Large amount of glass formed

At this point in the program approximately 60 tests had been conducted. A review of the total tests showed that the formulation which resulted in a product with the largest amount of glassification was 14% silicon, 14% aluminum, 27% silica, 15% barium dioxide and 30% potassium dioxide. Although a satisfactory glassified product could be made with this composition, the reaction rate was very rapid and splattering occurred. The hazardous materials mixed with the raw materials for encapsulation would also splatter during the reaction. Efforts were therefore directed to slow the reaction rate while retaining the high temperature and acceptable glassification.

The first attempts to slow the reaction rate were made by adding glass powder. While the reaction rate was slowed, the product contained little or no glass. Changes in the type and ratio of the fuels were tried along with the substitution of calcium dioxide for barium dioxide. Table 4 shows the results of these tests.

Compositions 4, 6, 11 and 12 produced the best glass product. Compositions 4 and 6 had some crystalline areas which could be undesirable in terms of resistance to leaching. Compositions 11 and 12 which produced excellent glass products had high reaction rates due to the high levels of barium dioxide. This first attempt at slowing the reaction was essentially a failure.

Several additional approaches to slow the pyrochemical reaction and optimize glass formation were assessed. The first concerned the particle size of the ingredients. Each ingredient was sieved to obtain the smallest possible mesh size. The mesh size of each material that was obtained is as follows:

silicon powder	200 mesh
aluminum powder	200 to 325 mesh
silica	240 mesh
barium dioxide	200 mesh
potassium dioxide	200 mesh

No discernable difference in reaction resulted from closer control of particle size. Several permutations of the dioxide content were investigated varying both percentage and the compound between potassium, calcium and barium dioxide. These tests only validated the prior observance that high barium or barium/potassium dioxide concentrations were required for glass formation. This was always associated with a fast reaction rate.

Elimination of the aluminum was tried to produce a lower melting temperature and slower reaction. No reaction produced a satisfactory glass product unless aluminum was used.

The final series of tests is detailed in Table 5. Clearly, reactions 1 and 2 gave the best glass products but with only some crystalization. The other reactions had lower reaction temperatures but did not produce a satisfactory glass product.

TABLE 4. MODIFICATIONS FOR SLOWER REACTION RATES

Sample No.	Compositions (%) Silicon powder	Aluminum powder	Silica	Calcium dioxide	Barium dioxide	Potassium dioxide	Results
1	17	17	27	11		28	Some glass
2	16	16	26	10.5		31.5	" "
3	20	20	33	13		13	Moderate amount of glass; crystallinity
4	18	18	29	23		12	Slow reaction; almost 100 % glass; large crystalline area
5	18	18	29		23	12	Little glass
6	13	13	33	27		13	Almost 100 % glass; some crystallinity
7	8	8	38	31		15	Did not react
8	12.5	12.5	25		25	25	Moderate amount of glass
9	12.5	12.5	12.5		37.5	25	Large amount of glass formed
10	14	14	7		50	14	" " " " "
11	8	8	8		69	8	Fast reaction; almost 100 % glass
12	7	7	20		60	7	Fast reaction; excellent glass product

TABLE 5. ADDITIONAL TESTS ON SLOW REACTING COMPOSITIONS

Sample No.	Compositions (%) Silicon powder	Aluminum powder	Silica	Glass powder	Barium dioxide	Calcium dioxide	Potassium dioxide	Results
1	6	6	17	12	53		6	Almost 100 % glass
2	7	7	21		64			Almost 100 % glass; temperature > 1100°C (> 2012°F)
3	6	6	10	12		56		No reaction
4	11	11	28		50			Slow reaction but no glass. Temperature 870°C (1598°F)
5	6	6	19	12	56			Moderate amount of glass. Temperature 900°C (1652°F)
6	21			14	64			Crystalline product. Temperature 260°C (500°F)
7	18	18		29		23	12	Small amount of glass. Temperature 930°C (1706°F)

In all of the compositions which gave good glass formation there was a tendency to devitrify in the center of the reacted compact. This was attributable to the slower cooling rate in that portion of the mass. This was not considered to be a major impediment and a decision was made to proceed with the program. It appeared necessary to establish the potential of this type of glassification to effectively encapsulate hazardous materials before trying to solve all the practical problems.

EVALUATION OF MATERIAL ENCAPSULATION

The use of glass encapsulation is restricted essentially to nonvolatile inorganic materials. To cover a range of material categories five test compounds were selected:

copper arsenate	antimony sulfide
cadmium selenide	ammonium dichromate
lead dihydroxydicarbonate	

They basically reflect toxic inorganic compounds containing heavy metal ions, but include materials that decompose below the temperature of the pyrochemical reaction (white lead and dichromate), an intermetallic (CdSe), and compounds that could take part in the glass reaction such as the arsenate and sulfide.

To evaluate encapsulation potential, a basic composition of 7% Al, 7% Si, 21% SiO_2, and 65% BaO_2 was selected. Violent reactions were experienced in the first attempts to incorporate lead carbonate or ammonium dichromate. To alleviate this problem, the composition was changed to one of 20% Al, 20% Si, 20% KO_2, and 40% CaO_2. The test materials were added to this blend as 10% to 33% of the weight of the total mix. These weight variations reflect an attempt to maintain a constant volume of 25% added impurity. The difficulties in measuring bulk densities made this an approximation. The large differences subsequently observed in leachate values showed close controls on volume ratios to be unimportant.

Compacts were prepared and reacted for each of the five test materials. With the exception of the cadmium selenide system, all compacts behaved as expected. There was some devitrification in the center of each of the reacted masses. The cadmium selenide charge, however, resulted in a porous clinker rather than a glass.

All test compacts were subjected to leaching studies. These were 48-hour exposures to boiling water in the Soxhlet apparatus. The averaged results of these tests are as follows:

Arsenic	5.0 mg/100ml of leachate (0.007 oz/gal of leachate)
Antimony	1.5 mg/100 ml of leachate (0.002 oz/gal of leachate)
Chromium	0.01 mg/100 ml of leachate (0.00001 oz/gal of leachate)

Lead	0.05 mg/100 ml of leachate (0.00006 oz/gal of leachate)
Selenium	1.70 mg/100 ml of leachate (0.002 oz/gal of leachate)
Cadmium	0.025 mg/100 ml of leachate (0.00003 oz/gal of leachate)
Copper	0.12 mg/100 ml of leachate (0.00002 oz/gal of leachate)

Those materials showing low levels in the leachate -- chromium, lead, and copper -- gave consistent results from test to test. For those with high concentrations in the leachate -- antimony and arsenic -- there was considerable scatter of data. Both selenium and cadmium gave consistent data even though the fusion and glass formation was poor.

The fusions had an undesirable side effect that overshadowed the positive results of encapsulation. In all fusions, material was released during reaction. Much of this was gas in the form of unreacted oxygen, but it carried with it particulate matter. The particulate deposited on the cold portions of the reaction chamber. Analyses showed that each of the deposits contained significant amounts of the material being encapsulated or a product of its thermal decomposition. The amount lost varied between 1% and 4% of the total reaction mass depending on the material being added to the basic system.

The release of such products could render the process impractical. Three adjustments were tried to alleviate the difficulty. The first approach was to increase the fuel-to-oxidizer ratio. This did not appreciably change the gas and particulate release, but it did diminish the efficiency of glass formation. In most cases, leachate losses increased in some as much as ten times. The second attempt replaced the KO_2 with oxidizers with greater thermal stability: BaO_2, CaO_2, $NaClO_3$. These gave little change in off gassing and also affected the glass formation.

The last approach was to include inerts, basically SiO_2, to slow the reaction down. This decreased the reaction temperature into the range of 800°C (1472°F). This was not high enough to form a good glass matrix.

The only other alternatives were gasless pyrochemical reactions or an external heat source. The chemical makeup of known gasless pyrochemical systems would allow formation of a refractory clinker but not a glass per se. The results with CdSe indicate that such an approach might be successful even though a porous structure might result. Using external heat either alone or in combination with a pyrochemical reaction also had possibilities. None of these approaches were pursued in this program.

SECTION 4

LIQUID SODIUM REACTIONS

BACKGROUND

The ability of liquid sodium to degrade a broad range of chemicals is well established. In analytical chemistry, a technique used to define organic material is based upon the knowledge that such materials are completely degraded with release of hydrogen as gas. With the use of liquid alkali metals as heat transfer fluids, knowledge has been gained on the behavior of foreign materials in contact with sodium and the fate of the decomposition products.

With the exception of hydrogen and nitrogen, all other elements that occur in toxic materials should be retained by the sodium. Some, such as carbon, will appear as particulates and can be filtered out. Others, such as oxygen, have temperature-sensitive solubilities and can be removed by thermal processes. Those elements that remain within the sodium are expected to be ultimately recoverable as innocuous materials such as sodium chloride, elemental metals, sodium sulfide, etc.

Systems to handle liquid sodium are items of commerce. Equipment and process technology are available to provide a liquid alkali metal system to degrade toxic materials. The questions that remain are the practicality of such a system, in terms of the controllability of the exotherms that may result and the ability to remove or otherwise recover the resultant degradation products in an acceptable form.

EXPERIMENTAL TECHNIQUE

The experimental apparatus used for laboratory tests was based upon the current practice for alkali metal systems. A schematic representation of the equipment is presented in Figure 2, with sections isolated for easier identification. The test unit consisted of seven separate components: 1) furnace and air blower, 2) alkali metal container/reactor vessel, 3) inert gas supply and circulation unit, 4) hazardous material reservoir/metering unit, 5) gas sampling system, 6) liquid metal sampling system, and 7) a cold leg in the bottom of the alkali metal container that provides a gradual transition from operating to ambient temperature (a cold trap). Each of these subsystems contain standard control and monitoring components necessary to measure base line conditions (temperature, electrical input, reactant in-flow and off gassing) and follow changes occurring during the test.

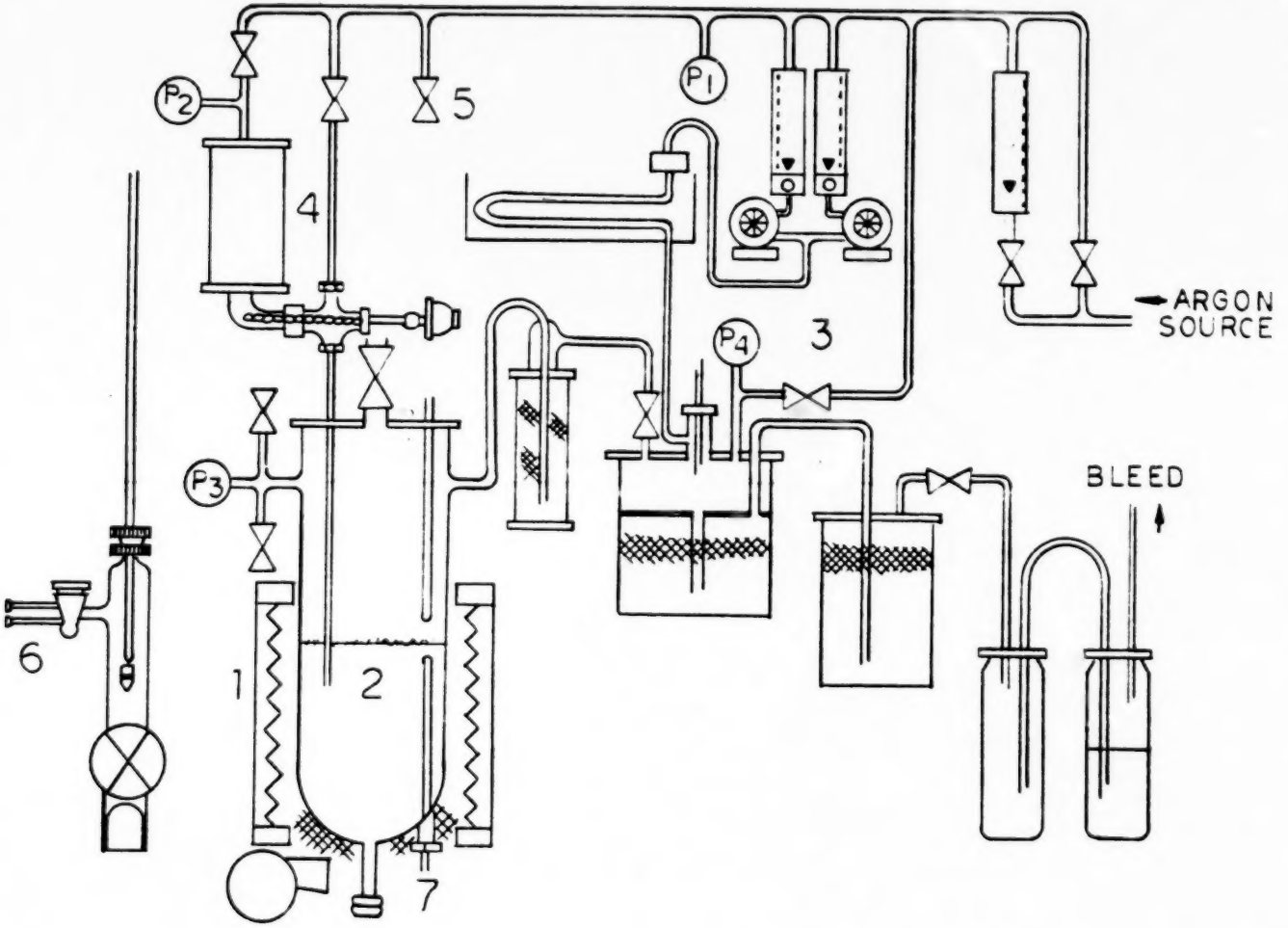


Figure 2. Experimental reactor and analysis system

All components in contact with sodium were constructed from 316 stainless steel using accepted practice. After assembly, the experimental system was cleaned and checked for leaks under argon pressure and vacuum. The reactor was charged with 1000 ± 20 g (35.3 ± 0.71 oz) of reactor grade sodium at 125°C (257°F). A stream of argon was injected into the sodium through a port about 15 cm (5.9 in.) below the sodium meniscus. This stream stirred the molten sodium, but its basic purpose was to act as a carrier gas and dispersing agent for the reactant materials.

Five materials were selected as representative hazardous materials: antimony trisulfide, mercuric chloride, sodium fluorosilicate, 2-chloro-4-phenyl phenol, and parathion. Kepone was added later. All test materials were obtained in particulate form except parathion which was liquid.

For the solids, approximately 100 g (3.53 oz) of each material was placed in the reservoir above the reactor, fed by a vibrator to an auger screw-feed, and then delivered to the recirculating, carrier stream of argon.

When the reactor was filled and considered ready for operation, the temperature profile of the system was monitored and a gas sample was taken using an evacuated glass bulb before the hazardous material was added. As the hazardous materials were added, gas samples were taken periodically to determine if gaseous products were formed. Gas analyses were made using a gas chromatograph.

The addition of hazardous material was interrupted at selected intervals during the test to remove samples of liquid sodium. These samples were taken by dipping a nickel bucket into the melt under an inert cover gas with a self-contained sampling head fitted to the top of the reactor. When the addition of the hazardous material was completed, gas and metal samples were taken while the system equilibrated. These samples were used to determine the extent of reaction. The sodium is dissolved in methanol and insolubles are filtered out. Standard chemical analysis is then employed for both the insoluble material and the solution.

Following equilibration the system was cooled and a core sample was taken by forcing a 1-cm-diameter (0.39 in.) tube from the top of the reactor, through the sodium to the bottom of the reactor. Sections were cut from the tube to provide samples that allowed the distribution of the reaction products in the sodium column to be determined. The cold trap at the bottom of the reactor provided samples to determine the degree of segregation of products due to temperature effects. The test results are summarized in Table 6. Observations of the individual reactions with molten sodium are discussed in the following section.

TEST RESULTS

Antimony trisulfide was the first material tested. It represented a toxic heavy metal material. Approximately 46 g (1.63 oz) of Sb_2S_3 was added at a rate of 0.2 g/min (0.007 oz/min), by means of a screw feed, into the recirculating stream of argon carrier gas.

TABLE 6. TEST DATA COLLECTED FROM REACTIONS OF HAZARDOUS MATERIALS WITH 1000 g LIQUID SODIUM IN STAINLESS STEEL REACTOR VESSEL

Test No.	1	2	3	4	5	6
Hazardous Material	Sb_2S_3	$HgCl_2$	Na_2SiF_6	$Cl_2C_6H_4$-C_5-H_4OH	$C_{10}Cl_{10}O$	$C_{10}H_{14}NO_5PS$
Amount Used	45.7 g (1.6 oz)	100.1 g (3.5 oz)	100.1 g 3.5 oz)	53.7 g (1.9 oz)	84.0 g (3.0 oz)	98.2g (3.5 oz)
Temperatures (°C)						
Sodium	310 ± 10 (590°F)	200 ± 10 (392°F)	210 ± 10 (410°F)	210 ± 10 (410°F)	245 ± 10 (473°F)	250 ± 10 (482°F)
Hazardous Material	15 (59°F)	14 (57°F)	15 (59°F)	23 (73°F)	25 (77°F)	27 (81°F)
Ar Cover Gas	15 (59°F)	14 (57°F)	15 (59°F)	23 (73°F)	25 (77°F)	27 (81°F)
Minimum Cold Leg	80 ± 5 (176°F)	75 ± 5 (167°F)	60 ± 10 (140°F)	70 ± 10 (158°F)	45 ± 10 (113°F)	55 ± 10 (131°F)
Ar Recirculation Rate	9.4 ℓ/min (2.5 gal/min)	9.4 ℓ/min (2.5 gal/min)	9.4 ℓ/min (2.5 gal/min)	9 ℓ/min (2.5 gal/min)	9 ℓ/min (2.5 gal/min)	9.4 ℓ/min (2.5 gal/min)
Bleed/Make-up Rate	0.09 ℓ/min (0.02 gal/min)	0.09 ℓ/min (0.02 gal/min)	0.12 ℓ/min (0.03 gal/min)	0.09 ℓ/min (0.02 gal/min)	0.14 ℓ/min (0.04 gal/min)	0.3 ℓ/min (0.08 gal/min)
System Pressure						
Equilibrium	1.07 atm	1.05 atm	1.02 atm	1.05 atm	1.2 atm	1.2 atm
Up stream	1.16 atm	1.10 atm	1.09 atm	1.17 atm	1.25 atm	1.8 atm
Down Stream	1.00 atm	1.00 atm	1.00 atm	1.00 atm	1.05 atm	1.2 atm
Heating Requirements						
System Equilibrium	4.73 Kcal/min (18.77 BTU/min)	4.31 Kcal/min (17.10 BTU/min)	4.15 Kcal/min (16.47 BTU/min)	4.66 Kcal/min (18.49 BTU/min)	5.01 Kcal/min (19.88 BTU/min)	4.44 Kcal/min (17.61 BTU/min)
During Reaction	4.73 Kcal/min (18.77 BTU/min)	3.30 Kcal/min (13.1 BTU/min)	4.30 Kcal/min (17.06 BTU/min)	3.94 Kcal/min (15.63 BTU/min)	1.86 Kcal/min (7.38 BTU/min)	2.87 Kcal/min (11.39 BTU/min)
Average Rate of Addition	∿0.02 g/min (∿ 0.001 oz/min)	∿3.4 g/min (∿ 0.12 oz/min)	∿2.9 g/min (∿ 0.10 oz/min)	∿0.95 g/min (∿ 0.03 oz/min)	∿0.4 g/min (∿ 0.01 oz/min)	∿1.2 g/min (∿ 0.04 oz/min
Sensible Heat of Reaction	0 Kcal/mol (—)	∿ 23 Kcal/mol (∿ 91 BTU/mol)	+9 Kcal/mol (+36 BTU/mol)	∿ 190 Kcal/mol (∿754 BTU/mol)	∿5800 Kcal/mol (∿ 23,016 BTU/mol)	∿690 Kcal/mol (∿2738 BTU/mol)
	0 Kcal/g (—)	-0.30 Kcal/g (-540 BTU/lb)	+0.05 Kcal/g (+90 BTU/lb)	-0.75 Kcal/g (-1350 BTU/lb)	-3.15 Kcal/g (-5670 BTU/lb)	-1.31 Kcal/g (-2358 BTU/lb)

Neither temperature nor pressure excursions were observed during the addition of the particulates. Hydrogen was found in the samples taken from the recirculating gas stream. It appeared at the same time that the Sb_2S_3 reaction started and the concentration increased from about 1% to 2% during the 225 minutes required for adding the Sb_2S_3. Its presence is attributable to moisture entrained on the Sb_2S_3.

Free antimony metal and sodium sulfide appeared to be the primary products. The liquid portion of the cold leg contained some sodium antimonate and a small amount of an unidentifiable substance. The analytical results indicate that the following reactions may contribute to the degradation of antimony trisulfide in molten sodium:

$$Sb_2S_3 + 6Na \rightarrow 2Sb + 3Na_2S$$
$$Sb_2S_3 + 9NaOH \rightarrow 2Na_3SbO_3 + NaHS$$
$$Na_2S + Sb_2S_3 \rightarrow 2NaSbS_2$$

Antimony is soluble in molten sodium up to 65 weight percent. Purification and recycle of the sodium would be accomplished by a two-step process: 1) cold trap filtration, to remove Na_2S and excess oxide and other insoluble materials, and 2) vacuum distillation, to recover antimony as a pure metal.

Mercuric chloride was the second material. It was used to represent a toxic heavy metal compound. The reactor temperature was reduced to 200°C (392°F) to minimize evaporation of mercury. Copper mesh and fiber glass filters were placed in the recirculating gas stream to remove any mist or vapors of mercury from the argon. Approximately 100 g (3.53 oz) of $HgCl_2$ was added to the sodium at a rate of about 3.4 g/min (0.12 oz/min).

No pressure increases were observed from the reaction of mercuric chloride and sodium, but there was a substantial heat of reaction. This sensible heat did not cause appreciable temperature increases in the reactor but was observed and measured as the reduction in the electrical energy required to maintain the temperature of the system. This "sensible heat of reaction" must be considered in construction and operation of a waste disposal unit.

Hydrogen was the only contaminant found in the recirculating gas stream. Its concentration was 0.2% after the first 5 minutes of the test and remained fairly constant, decreasing to 0.1% slowly during the 29 minutes of the mercuric chloride addition. Again, its presence is attributable to entrained moisture.

Analyses of dip samples and core samples of the sodium showed that the following reactions contribute to the degradation of mercuric chloride in molten sodium:

$$HgCl_2 + 2Na \rightarrow Hg + 2NaCl$$
$$xHg + yNa \rightarrow Na_yHg_x$$

The amalgam settles within the liquid layer. The salt migrates to the cooler regions, the surface, and the cold trap, where it crystallizes.

Elemental mercury was found in both filter traps and in the methanol wash solution. The mercury concentration within the molten sodium was greatest (3.1%) at the bottom of the reactor and within the top portion of the cold trap (5.6 to 5.9%).

Through analysis of methanol washings approximately 15% of the mercury added to the reactor could be accounted for as an amalgam with sodium. More than 80% was present in hard, metallic particles. These contained about 90% Hg, which corresponds to the peritectoid compound NaHg.

Chloride analyses of samples removed from the reactor showed between 7 and 15% NaCl on the surface and a maximum of 0.2% in the cold trap. This separation can be attributed to the low solubility of the salt and the density difference between it and sodium.

Mercury could be distilled from sodium but it is not a general industrial practice. The suggested disposal procedure would be to remove the NaHg compound in a cold trap/filter section, react the amalgam with alcohol to release the mercury for recovery, and neutralize the alcoholate for disposal. In a circulating system the NaCl would be expected to be removable by filtration also.

Sodium fluorosilicate was selected to represent a volatile inorganic chemical and a chlorine-bearing material. Approximately 100 g (3.53 oz) of Na_2SiF_6 pulverized and dried at >100°C (>212°F) prior to placing it in the reactor was added to molten sodium (210°C [410°F]) over a period of 34 minutes. The absence of hydrogen in the off gas confirmed the assumption that the hydrogen found in the recirculating gas stream in previous tests came from the moisture absorbed on the reactant powders. Neither pressure nor temperature excursions were observed as the fluorosilicate was added to molten sodium. It was necessary to use energy to maintain the temperature of the reactor in this test.

Analytical results indicate that the following reactions probably occur as the Na_2SiF_6 is added to molten Na:

$$Na_2SiF_6 + 2Na \rightarrow SiF_4 + 2NaF$$
$$SiF_4 + 4Na \rightarrow Si + 4NaF$$

These reactions have been verified in the investigations of production mechanisms for silicon for photovoltaic cells.

The sodium contained about 0.1 weight percent silicon in solution, which is similar to general experience where liquid sodium is exposed to a source of silicon. Samples from the surface of the sodium contained about 12.8% weight percent residue, 0.7% of which was pure silicon. X-ray diffraction patterns of this residue showed lines for sodium flouride only, indicating that the silicon was amorphous.

Analyses of the cold trap showed the presence of sodium fluoride, silicon, and some unreacted sodium fluorosilicate. A gas was evolved during the preparation of the sodium samples, but samples for analysis could not be obtained. It is probable that it came from thermal degradation of residual fluorosilicate.

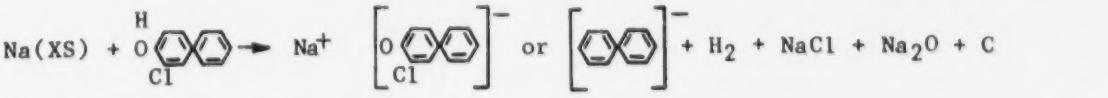
2-chloro-4-phenyl phenol was selected as representative of chlorinated aromatic organic compounds. Approximately 100 g (3.53 oz) of $C_{12}H_9OCl$ was added to molten sodium ($\sim$200°C [$\sim$392°F]) over a period of 63 minutes. The test was interrupted twice by an agglomeration of particles in the addition tube, which required disassembly and cleaning.

Although neither pressure nor temperature excursions were observed, a white powder was seen to be trapped in the recirculating gas filter. The general appearance of this powder and the larger particules filling the addition tube were similar to sodium phenoxide. Hydrogen was the only contaminant gas found in samples taken from the argon cover gas. Its concentration increased slowly to a maximum of 5.4% after the addition of 50.6 g (1.78 oz) of 2-chloro-4-phenyl phenol, after which it decreased slowly.

Ultraviolet analysis of solutions prepared from dip samples showed the presence of organic materials but no evidence of the phenyl phenol. These appeared to be partial decomposition products. The plugging problem during material addition could be explained by a rapid, exothermic reaction. Reactions could produce solids such as sodium phenoxide which prevent further interaction between the sodium and the phenol.

The reactor temperature was maintained, and the recirculation of argon continued for 18 days. Free carbon was found in samples taken after 6 and 18 days, indicating that decompositon was proceeding slowly. Ultraviolet analyses of these later samples continued to show the presence of organic material, but there was a significant decrease in concentration between the sample taken after 6 days and that taken after 18 days.

Analyses of the samples taken during this test indicate that the degradation reaction of 2-chloro-4phenyl phenol with molten sodium progresses through several stages. The exact nature of the reactions and additional compounds that may be formed is unknown. The following series of product intermediates may be used to describe the results:



Continued reaction at 210°C (410°F) decomposed some of the basic ring structure, and released the elemental carbon.

The disposal procedure would be similar to those described previously. Both the salt and carbon produced in the reaction would be removable in cold trap filters. Excess sodium would be vacuum distilled from these products and returned to the reactor. The residue would be neutralized and diluted for standard disposal procedures.

Parathion (0,0'diethyl 0-p-nitrophenyl phosphorothioate) was the only liquid material used in this program. Approximately 98 g (3.55 oz) was added to the sodium in the reactor, at a rate of about 0.97 ml/min (0.03 oz/min). It was injected into the sodium via a hypodermic syringe through a separate port. The argon was recirculated for stirring but did not carry the parathion.

Neither temperature nor pressure excursions occurred as the parathion was added. The operating pressure within the reactor increased slowly through the 82-minute test, to approximately 1.6 atm. The increase was attributed to the formation of a crust on the molten sodium and to the entrainment of particulates in the gas filter trap.

A considerable amount of hydrogen was released from this reaction. During the addition of the first 25 g (0.88 oz) of parathion the concentration in the recirculating gas stream increased to a maximum of about 8.6%. The concentration held constant for the next 25 g (0.88 oz) addition. It had decreased to 6.7% after 90 g (3.17 oz) had been added. A combination of hydrogen permeability, greater system pressure, and extensive sampling reduced this concentration to 2.5% when all the parathion had been added.

Ethene was also found in all gas samples taken after parathion was added to the sodium. Three other, unidentified, light hydrocarbons were detected. It should be noted that these were detected in the gas issuing from the reactor. They did not persist through the NaK bubbler used to repurify the argon for recirculation.

Analysis of sodium samples taken from the reactor showed approximately 0.5 ppm unreacted parathion. Carbon particles were found on the surface and at the bottom of the reactor. Neither sulfur not phosphorus-containing species could be detected in the gas phase. The sulfur was retained in the sodium as Na_2S. The fate of the phosphorous could not be adequately defined.

Surprisingly, nitrogen was not found in the off gas. This could not be explained.

Because Kepone (decalone) was of immediate concern to EPA, during the course of this program it was added to the list of test chemicals. Approximately 84 g (3 oz) of commercial material was added to molten sodium at 250°C (482°F) over a period of 312 minutes. The addition of Kepone created an exotherm that significantly reduced the amount of energy required to maintain the operating temperature.

The degradation reaction formed sodium chloride and free carbon. These concentrated on the surface of the sodium and interferred with dip samples and with the reaction of the Kepone added later in the test. As a result, small quantities (< 12 ppm) of Kepone were detected in the samples containing the greatest proportions of the reaction products. Some hydrogen was generated from moisture absorbed on the Kepone but no free halogen was found in the gas phase.

Degradation of Kepone appeared to follow a progressive reaction pattern similar to that observed with the phenyl phenol. No effort was made to identify the inbtermediate reaction products but the gas chromatograph gave 11 peaks, in addition to that of the parent compound. These all appeared to be partially chlorinated materials, with concentrations less than 1 ppm. A total of about 1 g (0.04 oz) of Kepone could be identified as remaining in the reactor after terminating this test. It is expected that continued reaction would ultimately reduce all added material to carbon, sodium chloride, and hydrogen.

A soil sample was the final test sequence run in the sodium tests. it employed soil taken at the Evans City Plant of MSA. This test was run to observe the behavior of soil added to the liquid sodium. Due to the complexity of the soil sample, no attempt was made to determine the solid products which might be formed by reaction with sodium.

The sample was pulverized and coarse stones removed to provide a form suitable for the feed mechanism of the system. The soil was not dried or treated in any other manner.

The mechanism of addition to the sodium and the rate were the same as those used for the solid candidate chemicals. One hundred grams (3.5 oz) of material was added over a 25 minute period. There was no measurable increase in the temperature of the system during the total time of soil addition. The principal observation was a sharp increase in the hydrogen concentration in the cover gas. Concentrations approaching 10% by volume were observed.

The hydrogen can be attributed to the moisture content of the soil but it is reasonable to conclude that organic materials in the soil are also contributing. Dip samples showed traces of carbon and the cold leg contained a concentration of sodium oxide at its interface with the pot.

Core samples showed that the majority of the soil added had settled to the bottom of the pot. Analysis of the methanol solution used to dissolve the sodium and the residues would not indicate that there was any appreciable conversion of soil components to forms soluble in methanol or water.

This test would indicate that soils could be added to liquid sodium along with the materials to be degraded without any adverse effect on the chemical process. The soils and the oxides formed by sodium reaction with entrained water can be expected to complicate the cold trap and filtration system. Large quantities of inerts would rapidly overwhelm and plug the system.